

Lowering the hydrogen desorption temperature of NH_3BH_3 through B-group substitutions

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We present *ab initio* results for substitutions in the promising hydrogen-storage material NH_3BH_3 to lower its hydrogen desorption temperature. Substitutions have already been investigated with significant success recently, but in all cases a *less* electronegative element is substituted for the *protic* hydrogen in the NH_3 group of NH_3BH_3 . We propose a different route, substituting the *hydridic* hydrogen in the BH_3 group with a *more* electronegative element. To keep the gravimetric density high, we focus on the second period elements C, N, O, and F, all with higher electronegativity compared to H. In addition, we investigate Cu and S as possible substitutions. Our main results include Bader charge analyses, hydrogen binding energies, and kinetic barriers for the hydrogen release reaction in the gas phase as well as in the solid. While the different substituents show varying effects on the kinetic barrier and thus desorption temperature—some overshoot our goal while others have little effect—we identify Cu as a very promising substituent, which lowers the reaction barrier by approximately 37% compared to NH_3BH_3 and thus significantly influences the hydrogen desorption temperature.

1 Introduction

One of the greatest technical challenges facing society is the need to end our dependence on fossil fuels. Shifting to hydrogen as an alternative energy carrier presents an ideal solution, but is not yet practical, as its storage is one of the remaining bottlenecks in the technology.^{1,2} While conventional pressurized tanks cannot safely store hydrogen at sufficient density to be used as an equivalent substitute for gasoline in mobile applications, incorporating the hydrogen into the molecular structure of a material might reach the required density target set by the DOE.^{3–5} Amongst such materials, ammonia borane (NH_3BH_3 or AB) has been the subject of myriad studies and is one of the most promising hydrogen storage materials with a gravimetric storage density of 19.6 mass%.^{6–11}

Unfortunately, besides its favorable gravimetric hydrogen storage density, NH_3BH_3 starts to release its hydrogen only at elevated temperatures (12 mass% above 140°C, corresponding to the release of one H_2 per NH_3BH_3 unit).^{12,13} One of the most notable advances in this area was the substitution of a protic hydrogen in the NH_3 group with a Group I metal to form an alkali-metal amidoborane ($\mathcal{M}\text{NH}_2\text{BH}_3$ where $\mathcal{M} = \text{Li, Na}$).⁶ These materials demonstrate hydrogen desorption temperatures significantly lower than that of NH_3BH_3 —90°C with 10.9 mass% and 8.9 mass% for Li and Na, respectively. However, a further lowering is desirable, as for instance, the maximum operating temperature for a proton-exchange membrane fuel cell is 80°C.¹⁴

To this end, we propose a similar, albeit different, modification to the material's molecular structure. Rather than substitute a metal for a protic hydrogen in the NH_3 group, we instead replace a hydridic hydrogen in the BH_3 group with a more electron-accepting element. To keep the gravimetric density high, our obvious choices are the second period elements with the corresponding electronegativities C (2.55), N (3.05), O (3.44), and F (3.98), all higher than the value of 2.20 for H.¹⁵ We also consider using S (2.58) and Cu (1.90) as substituents. Cu is included because its single 4s electron (but otherwise closed shells) makes it electronically similar to H. The electronegativity of Cu is actually lower than that of H, but we find that in the monomer, Cu still prefers to bind to the BH_3 group rather than the NH_3 group by 0.19 eV. We include S for reasons that will be elaborated on later. Note that these kinds of substitutions have not yet been tried in the hydridic group, as their synthesis is more complicated.* Also note that substitutions of the protic hydrogen in the NH_3 group are more straightforward in principle and “less intrusive” to the electronic structure, as all alkali metals have a single s electron in their outer shell and H has already the highest electronegativity of all alkali metals. On the other hand, our proposed substitutions of the hydridic hydrogen in the BH_3 group are likely to create radicals and constitute an unconventional and major rearrangement of the bonding and charge density in the entire molecule. Nonetheless, according to our calculations, all substitutions create stable molecules with a negative cohesion energy

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and no imaginary modes in their vibrational spectra, indicating that their synthesis is in principle possible.

Several studies have aimed to investigate the hydrogen desorption mechanism for both NH_3BH_3 and the alkali-metal amidoboranes using experimental, density functional theory, and quantum chemistry methods.^{12,16–21} The computational parts of these studies have focused mostly on the interactions of molecules in the gas phase. We aim here to take full advantage of density functional theory in a plane-wave implementation and study not only gas-phase effects, but also the release and formation of molecular hydrogen in the solid state, taking into account the effects of nearby molecules on the reaction. To this end, this manuscript is organized into two main sections: First, we examine only gas-phase structures in order to validate our methods as well as filter out substituents from our list that yield less desirable results. Then, we perform calculations in the solid phase, again filtering out substituents, and encourage the synthesis of the structures that show improved hydrogen desorption properties compared to NH_3BH_3 .

2 Computational Details

We have performed *ab initio* calculations at the density functional theory (DFT) level, as implemented in the plane-wave code VASP (version 5.3.3).^{22,23} Since ammonia borane is a strong van der Waals complex,^{24,25} it is crucial to include van der Waals forces in our simulations. Thus, all calculations have been performed with the vdW-DF1^{26–29} exchange-correlation functional (i.e. revPBE exchange and LDA correlation in addition to the truly nonlocal correlation) with PAW pseudopotentials and an energy cutoff of 500 eV. Calculations in the gas phase were done in a 12 Å cubic box at the Γ -point. All structures were optimized until the forces on each atom were less than 1 meV/Å. All calculations were performed spin-polarized, as some of our substitutions result in unpaired electrons.

In the solid, structure searches have been carried out using the Universal Structure Predictor: Evolutionary Xtallography (USPEX),^{30–32} with structural optimizations done in VASP. We performed structure searches with two molecules per unit cell to correspond with the ground state structure of pure AB. In addition to these randomly-generated structures, we also included seed structures generated by modifying the low-temperature phase of pure AB. Each search spanned five generations, totaling over 150 structural optimizations per substituent. Because lattice parameters were allowed to (and did) vary, k-point meshes differed between structures, but their density was kept constant, i.e. the number of k-points k_i in a given reciprocal space dimension was given by $k_i = (0.1 \times l_i)^{-1}$ where l_i is the length of a lattice vector. Each of these structures was optimized until all ionic forces dropped below 10 meV/Å.

Nudged elastic band (NEB) calculations were also performed in VASP, utilizing the climbing image implementation from the VTST Tools package.^{33,34} For the solid phase, these calculations were performed on $2 \times 2 \times 2$ supercells to minimize finite-size effects, with either 5 or 7 intermediate images, each converged to forces of less than 50 meV/Å.

At low temperatures (0 ~ 225 K), NH_3BH_3 exhibits an or-

Table 1 Binding energies (eV) of atoms in gas phase molecules $\text{NH}_3\text{BH}_2\mathcal{X}$ with $\mathcal{X} = \text{H}, \text{F}, \text{O}, \text{S}, \text{Cu}$. H itself is not a substitution, resulting in the original NH_3BH_3 molecule, but is given here for reference. Atom designations correspond to those in Fig. 1 and substituent atoms always replace the H in position B3.

\mathcal{X}	N1	N2	N3	B1	B2	B3 ^{sub}
H ^{ref}	-4.140	-4.140	-4.140	-4.592	-4.592	-4.592
F	-4.137	-4.138	-4.138	-4.609	-4.609	-6.962
O	-4.296	-4.297	-4.297	-1.058	-1.058	-6.120
S	-3.924	-4.175	-4.175	-1.982	-1.982	-4.336
Cu	-2.638	-2.610	-2.610	-4.391	-4.391	-2.659

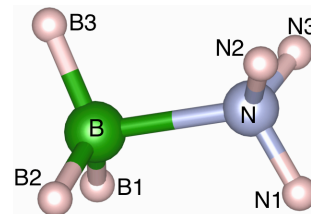


Fig. 1 Diagram of an NH_3BH_3 molecule, including designations used to refer to each H atom. All substitutions have been done at the B3 position.

thorhombic structure with space group $Pmn2_1$. Heated above 225 K, it undergoes a phase transition to a body-centered tetragonal structure with space group $I4mm$. In both cases there are two NH_3BH_3 molecules per conventional unit cell and the main difference is that the N–B backbone of the molecules are parallel in the high-temperature phase, while they are slightly tilted with respect to each other in the low-temperature phase. Although we are mostly interested in hydrogen desorption at room temperature or higher, unfortunately, the high-temperature phase is not accessible for standard transition state searches, as it tries to relax towards the low-temperature phase. As such, all our calculations are done in the low-temperature phase.

3 H_2 desorption in the gas phase

3.1 Structure analysis

The first step in examining these prospective materials resulting from our proposed substitutions is optimizing the molecules's structures in the gas phase. For the purposes of this investigation, we are only interested in materials with hydrogen desorption properties similar to those of AB, so we preferentially selected only the substituents that formed $\text{NH}_3\text{BH}_2\mathcal{X}$ molecules, retaining AB's original molecular shape, to continue study. We eliminated C and N from our original candidate pool at this stage because simple structural optimizations indicated that these substitutions did not allow for the formation of the $\text{NH}_3\text{BH}_2\mathcal{X}$ geometry. Those substitutions, due to their strong radical nature, resulted in a complete rearrangement of atoms in the BH_3 group. Also note that for each of the substituents used, our calculations indicate that substitution is energetically favorable in the B-group relative to substitution in the N-group of an isolated molecule.

We next found binding energies for each atom in gas phase

Table 2 Bader charge analysis (in units of e) for isolated gas phase molecules of $\text{NH}_3\text{BH}_2\mathcal{X}$. Numbers given demonstrate the change in charge after the substitution is made at position B3 and reflect the number of electrons gained relative to the neutral atom.

\mathcal{X}	N1	N2	N3	N	B	B1	B2	B3 ^{sub}
H ^{ref}	-1.00	-1.00	-1.00	2.96	-3.00	0.99	1.01	1.03
F	-1.00	-1.00	-1.00	2.97	-3.00	1.04	1.03	0.97
O	-1.00	-1.00	-1.00	2.94	-3.00	0.88	0.87	1.30
S	-1.00	-1.00	-1.00	3.00	-3.00	0.98	0.98	1.03
Cu	-1.00	-1.00	-1.00	3.01	-2.47	1.12	1.12	0.22

molecules with O, F, S, and Cu substitutions, given in Table 1. We expect that a successful substitution would lower the strength with which H atoms bind to the molecule, making this information a crude indication of the magnitude of a substituent’s effect on the molecule. The F substitution appears to have little effect on the binding energies compared to the H reference, while O, S, and Cu elicit significant changes. O and S reduce the binding energies of H atoms on the B side of the molecule whereas, interestingly, Cu affects the N side more significantly.

Although charge partitioning schemes are not unique, one can gain insight into the reasons for these changes in binding energies by looking at the Bader charge analysis (shown in Table 2) of an isolated molecule in gas phase. As expected, in the pure AB case, B donates three electrons to the H atoms bound to it and N takes the 3 electrons from the H atoms bound to it, but there is very little charge transfer between the two ends of the molecule. In this picture, H atoms in the B group are nearly perfectly accepting one electron. F and S substitutions do little to change the picture, but O and Cu substitutions have stronger effects.

The O atom takes a greater share of the charge from the nearby H atoms, resulting in a large decrease in these H atoms’ binding energies and a correspondingly large decrease in the gas phase H_2 desorption barrier (see section 3.2 and Table 3). While this is the desired effect, it is actually overshooting to a point where the O-substituted molecule becomes unstable in the solid phase, releasing hydrogen near 0 K. We would expect that S would produce a similar, but less pronounced effect in terms of altering the molecule’s electronic structure. The charge analysis and binding energies support this hypothesis, with S taking more charge than its neighbor H atoms and significantly lowering these H atoms’ binding energies, although displaying a higher H_2 desorption barrier (again, see Table 3). Clearly, the overall effect of these substitutions cannot be fully explained with changes in the molecule’s charge density or binding energies.

Where O and S caused a decrease in the binding energies of H atoms in the B group, Cu substitution results in a decrease of binding energies for H atoms in the N group. The Cu substitution’s effect on the Bader charge is similarly distinctive, with B only donating 2.47 electrons, of which Cu takes only 0.22.

3.2 H_2 release barriers in the gas phase

In the gas phase, we performed NEB calculations to find the amount of energy required to remove two H atoms from NH_3BH_3 to produce NH_2BH_2 and H_2 as well as the corresponding reac-

Table 3 Hydrogen desorption barriers (eV) from a single gas-phase molecule of $\text{NH}_3\text{BH}_2\mathcal{X}$ resulting in $\text{NH}_2\text{BH}\mathcal{X}$ and H_2 .

\mathcal{X}	gas phase H_2 desorption barrier [eV]
H ^{ref}	1.706
F	1.675
O	1.014
S	1.812
Cu	1.697

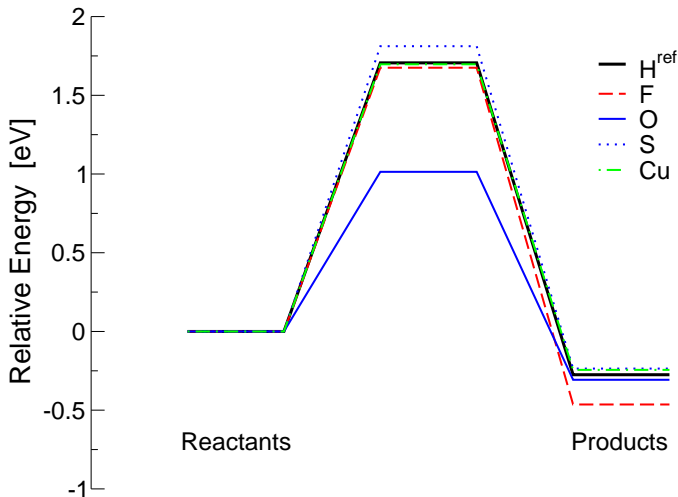


Fig. 2 Illustration of the kinetics and thermodynamics in the desorption of H_2 from $\text{NH}_3\text{BH}_2\mathcal{X}$ with $\mathcal{X} = \text{H}, \text{F}, \text{O}, \text{S},$ and Cu in the gas phase.

tion in substituted $\text{NH}_3\text{BH}_2\mathcal{X}$; results are collected in Table 3 and Fig. 2. In the standard AB molecule, the 1.706 eV barrier compares very well with the 37 kcal/mol ≈ 1.6 eV barrier found previously at the CCSD(T)/complete basis set (CBS) level of theory,¹⁹ as well as other DFT methods.¹⁶ The most apparent change here is the aforementioned barrier decrease for the O substitution. Whereas other substitutions alter the barrier by no more than 0.1 eV, O causes a drop of about 0.7 eV. Notably, the resulting barrier is almost the same as the binding energy for B1 and B2 hydrogen in the molecule (see Table 1).

In addition to the kinetic reaction barriers, Fig. 2 also reveals the thermodynamics of the hydrogen release reaction. Our value for ΔH in pure AB is in very good agreement with numbers in the literature (-0.28 eV versus -0.25 ,¹⁸ -0.29 ,³⁵ and -0.30 ³⁶). We find that the reaction is slightly exothermic in all cases and most substituents result in an energy release of approximately 0.25 to 0.30 eV per H_2 and AB molecule; only the F substitution is slightly more exothermic at 0.46 eV.

While decreasing the H_2 desorption barrier for an isolated molecule is a good indication of improved desorption properties, a better indication is how the material performs in the solid, which we discuss next.

4 H_2 desorption in the bulk

Other studies have focused on hydrogen desorption of monomers and dimers in the gas phase of NH_3BH_3 .^{16,19} However, with a

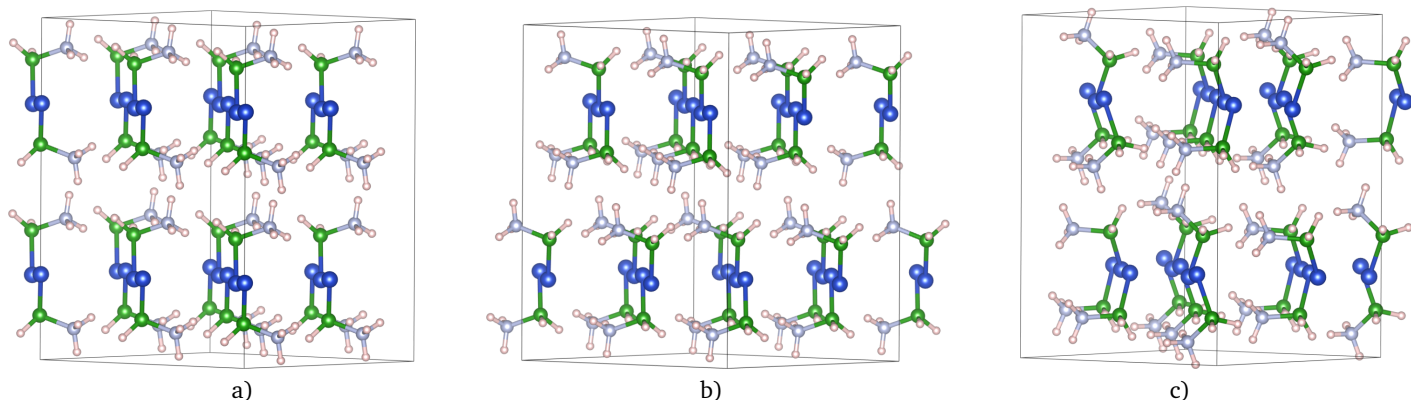


Fig. 3 Structures found for the Cu-substituted material and used to calculate the H_2 desorption barriers given in Table 5. Structure (a) is a supercell of the structure resulting from the randomized structure search. (b) and (c) are stable modifications only possible in a larger unit cell. All three structures are within ~ 50 meV per molecule energetically and could potentially coexist in the solid, while also maintaining the geometry of NH_3BH_2 . Blue atoms are Cu, green are B, purple are N, and pink are H.

plane-wave implementation of DFT we have the ability to find transition states for hydrogen desorption in the solid phase of NH_3BH_3 , which is what we ultimately want to know, accounting for effects of the entire environment on the reaction.

4.1 Structure search

None of the proposed substituted structures $NH_3BH_2\mathcal{X}$ have been synthesized as of yet. Therefore, we must find a prospective ground-state structure to simulate the hydrogen desorption reaction. To that end, we first performed an initial directed structure search for F, O, Cu, and S substitutions by modifying the experimental low-temperature ground state of AB. The F, Cu, and S substitutions resulted in (meta)stable candidate structures that we could use to estimate desorption barriers, with no imaginary frequencies in their vibrational spectra. We will include results for these structures in the following tables, but show them with asterisks in order to indicate that these structures are derived from NH_3BH_3 . The O substitution produced a structure where the $NH_3BH_2\mathcal{X}$ molecule is not computationally stable, with H_2 desorption occurring spontaneously during structural optimization. From this result, we can say that an O substitution seems to make some of the H atoms in the molecule easier to access (as already evident from Table 1), however the effect is too strong. This is the reason S was included in the list of possible substituents; we want to lower the barrier to H_2 desorption, and ideally the effect of S would be similar to, but less pronounced than that of O.

In addition, we have also performed a randomized structure search using the USPEX package. A first search was done with plain AB, verifying that the method found the experimental low-temperature ground-state structure.³⁷ Further searches were done for F, O, Cu, and S substitutions. The primary objective of these searches was to find structures that maintained the basic geometry of the original NH_3BH_3 molecule, for best comparison with un-doped AB as they are more likely to retain the hydrogen desorption properties of AB. Searches with F, O, and S substitutions found that the most energetically favorable structures significantly deviate from the desired molecular geometry. For this reason, we only show the Cu structures used (see Fig. 3), which

Table 4 Bader charge analysis for solid-phase structures of $NH_3BH_2\mathcal{X}$. Numbers given demonstrate the change in charge after the substitution is made at position B3 and reflect the number of electrons gained relative to the neutral atom. An asterisk indicates that results are given for a structure derived from the pure NH_3BH_3 structure, which may not be the absolute ground state.

\mathcal{X}	N1	N2	N3	N	B	B1	B2	B3 ^{sub}
H ^{ref}	-1.00	-1.00	-1.00	3.07	-3.00	0.98	0.98	0.97
F*	-1.00	-1.00	-1.00	3.07	-3.00	1.03	0.97	0.93
S*	-1.00	-1.00	-1.00	3.11	-3.00	1.02	1.05	0.83
Cu	-1.00	-1.00	-1.00	3.11	-2.04	1.05	0.99	-0.11

clearly maintain the NH_3BH_2 geometry we want to preserve.

Table 4 presents a Bader charge analysis for the solid structures, similar to that done on the gas phase structures in Table 2. Most notably, Cu atoms become electron donors in the solid rather than acceptors.

4.2 H_2 release barriers in the bulk

While the precise desorption pathways for AB have long remained mysterious, the simplest form of this reaction could in general occur in two ways: either two H atoms come together from opposite ends of an AB molecule to form H_2 in an intramolecular reaction, or H_2 could form from H atoms in neighboring molecules in an intermolecular reaction. One recent theoretical study¹⁷ used enthalpy of formation calculations to conclude that intermolecular desorption pathways are more energetically favorable, but did not consider kinetic barriers. Another study³⁸ performed molecular dynamics simulations, observed an intramolecular desorption event, and found an energy barrier for the process, but did not consider intermolecular processes. A more recent experiment found that AB molecules polymerize in a “head-to-tail” manner through a dehydrocyclization reaction,¹³ concluding that initial H_2 desorption occurs through intermolecular interactions. We consider both possibilities. We have performed NEB calculations to find the energy barrier to both intra- and inter-molecular forms of H_2 desorption. These calculations were performed in a $2 \times 2 \times 2$ supercell in order to minimize inaccuracies from mirror-

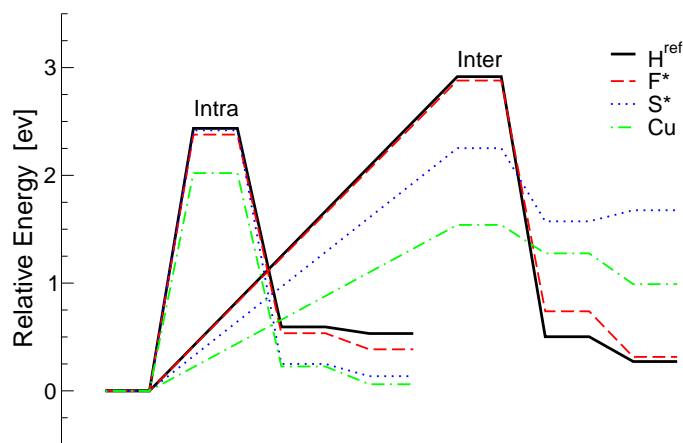


Fig. 4 Illustration of the kinetics and thermodynamics in the desorption of H_2 from $\text{NH}_3\text{BH}_2\mathcal{X}$ with $\mathcal{X} = \text{H}, \text{F}, \text{O}, \text{S}$, and Cu in the solid phase via intra- and inter-molecular pathways, resulting in one molecule of H_2 in the supercell, with the two plateaus at the end of the reaction indicating the relative energy of the system before and after the H_2 molecule diffuses out of the material.

Table 5 Hydrogen desorption barriers in the solid phase of $\text{NH}_3\text{BH}_2\mathcal{X}$ resulting in one interstitial molecular H_2 in the solid. An asterisk indicates that results are given for a structure derived from the pure NH_3BH_3 structure, which may not be the absolute ground state.

\mathcal{X}	bulk H_2 desorption barrier [eV]	
	intra-molecular	inter-molecular
H^{ref}	2.436	2.916
F^*	2.378	2.880
S^*	2.418	2.252
Cu	2.021	1.540

image effects. We have considered many possible combinations of H atoms and pathways for each reaction and the lowest barriers found in each category are shown in Table 5 and Fig. 4. The two end-points shown in Fig. 4 represent the relative energetics of the system before and after the H_2 molecule diffuses out of the material. There could be a small barrier for diffusion, which we did not consider.

From our transition-state searches in pure AB, we find support for the conclusion¹⁷ that the inter-molecular desorption process is more thermodynamically favorable, but we also find significantly lower kinetic barriers (shown in Table 5) for the intra-molecular reaction, indicating that the intra-molecular process is more likely to occur than the inter-molecular process. We further find that these barriers are larger than those found for the gas-phase molecules, and that this holds true for each substituent except Cu. The additional height of these barriers is due to disruption of the material's dihydrogen bond network, which is much more rigid in the low-temperature phase we are using for our simulations. In a previous study,³⁹ we found that significant barriers to disrupting this network (by rotating molecules, for instance) do not exist in the room-temperature phase of pure AB, where the desorption reaction occurs experimentally.

However, the most striking result in Table 5 is that the kinetic barrier for inter-molecular H_2 desorption in the Cu-substituted

material is significantly lower than that of standard AB, even lower than that of an isolated molecule. Figure 4 shows that the reaction is more endothermic than the other desorption processes studied, but the kinetic barrier is about 37% lower than that found for pure AB. Even allowing for a more complex decomposition mechanism in pure AB, we thus conclude that $\text{NH}_3\text{BH}_2\text{Cu}$ likely has a significantly decreased H_2 desorption temperature and is a very promising hydrogen storage material that could potentially fulfill the required DOE targets³ if it can be synthesized.

5 Conclusions

We examine the effects of substituting C, N, O, F, S, and Cu for one protic H atom in the BH_3 group of AB by simulating H_2 desorption barriers in both isolated molecules and solid structures. While some of the substituents result in structures that were not interesting to us or were undesirable—for example, O substitution creates a stable molecule, but shows spontaneous H_2 desorption when put together to form a solid—we found that the Cu substitution is very promising. It lowers the hydrogen desorption barrier significantly compared to pure AB, potentially improving on an already attractive hydrogen storage material. We thus encourage the synthesis of $\text{NH}_3\text{BH}_2\text{Cu}$ so that the possibility can be tested.

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